

ITEM No. 8,22

FILE No. XXIV - 19

21632

COPY No. 7

Copies sent to
Min Corbett
Min Ogile.
GE 3 (Chem)
GE 3 (E. Pet)
File copy.

RESTRICTED

151

ANORGANA G.M.B.H. WERK GENDORF

ARMED
FORCES

JAN 31 1950

MEDICAL
LIBRARY

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

RESTRICTED

ANORGANA GmbH WERK GENDORF

GENDORF, GERMANY

MISCELLANEOUS CHEMICALS

18-19 May 1945

Reported by:

V.C. BIDLACK - TIIC Chemicals
F. J. CURTIS - CWS, Hq ETOUSA
J. M. HARRIS - CWS, Hq ETOUSA

12 June 1945

CIOS Target Numbers 8/86, 22/1 (f), 22/534
⑧ Chemical Warfare

COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE
G-2 Division, SHAEF (Rear) APO 413

RESTRICTED

TABLE OF CONTENTS

<u>Subject</u>	<u>Page No.</u>
1. General -----	3
2. Chemicals Manufactured from Acetylene -----	9
3. Chemicals Projected from Acetylene -----	19
4. Application Data on Surface Coatings-----	27
5. Pharmaceuticals-----	28
6. Miscellaneous Items-----	31
7. Charts -	
Acetylene + Formaldehyde -----	33
-Butyrolactone -----	35
Acetylene + Acetaldehyde -----	37

PERSONNEL OF INSPECTION TEAM

Lt. Col. P.R. TARR-----	CWS, Hq ETOUSA
Col. J. H. ROONEY-----	M. of S.
Lt. Col. S.B. CORMACK--	M. of S.
Lt. Col. J.W. CRAWFORD-	M. of S.
Major T. LOVE-----	M. of S.
Major H.N. RYDON-----	M. of S.
Mr. V. C. BIDLACK-----	CWS, Hq ETOUSA
Mr. F. J. CURTIS -----	CWS, Hq ETOUSA
Mr. J. M. HARRIS-----	CWS, Hq ETOUSA
Mr. I. H. JONES-----	Petroleum Attache
Mr. G. M. KLINE-----	OD, Hq ETOUSA
Mr. E. B. PECK -----	Petroleum Attache

ANORGANA GmbH

WERK GENDORF

MISCELLANEOUS CHEMICALS

1. GENERAL

Anorgana GmbH was started as a subsidiary of I.G. Farbenindustrie AG in June, 1940 and financed by Montan Industrie Werke AG, a subsidiary formed by the German Government to handle such matters. The cost of construction was 120,000,000 marks. During the war and while construction was going on 4000 workers were employed, partly foreign. It is estimated that normally 2000 workers would be needed for full operation and for the present situation about 1000 could be used.

a. Organization

Names and positions of officials of the Anorgana GmbH:

Managing director	---	Dir. Dr. M. Wittwer
Inorganic department	---	Dr. M. Gruber
Organic department	---	Dr. G. Hagen
Sales Service department	---	Dr. J. E. v. Klenck
Accounting	---	W. Jansen
Social department	---	Dr. E. Lederle
Ordinance department	---	Supt. K. Wurzler

Name and position of official of I.G. Farbenindustrie AG:

Research and pharmaceuticals --- Dir. Dr. W. Reppe

b. Present Daily Manufacture

Leonil (detergent)	-	300 kg
Luphen (lacquer)	-	1,000 kg
Ether (narcotic)	-	250 kg
Ethylchloride techn.	-	3,000 kg
Ethylchloride pro narcose-		250 kg

c. Raw Materials and Finished Products on Hand

Common salt	2.477 tons	Formaldehyde 30%	30 tons
Barium carbonate	354 "	Ethylene oxide	52 "

Soda	65.4 tons	Aluminum chloride	61 tons
Sodium bisulphite		Copper sulphate	2.5 "
as SO ₂ 100%	19 "	Adipic acid	30 "
Hydrochloric acid		Ethylglycol	11 "
as HCl 100%	36 "	Ceresin	2.5 "
Graphite	290 "	Urea techn.	5 "
Mercury	62.7 "	Resin	6.7 "
Sulphuric acid as		Naphthlene	2 "
SO ₃	127 "	Octadecylalcohol	2.5 "
Chlorine	90 "	Castor oil	9.3 "
Caustic soda in		Sesame oil	20 "
solution as 100%	350 "	Rape-seed oil	4.5 "
Ferrous sulphate	32.5 "	Olive oil IIIrd	
Nitric acid 62%	8.4 "	quality	4.5 "
Methylated spirit	270.4 "	Paraffin	20 "
Phenylglycine	43.6 "	Stearic acid	11.6 "
Coke	80 "	Benzene	48 "
Diethylbenzene	122 "	Active carbon	5 "
Sulphur	950 "	Orthodichloro-	
Chloride of lime	27 "	benzene	15 "
Caustic potash	10 "	Carbon tetra-	
Calcium chloride	10 "	chloride	2.5 "
Methanol	0.3 "	Phosphorus-	
Ethylene chloride		trichloride	2.3 "
crude	171 "	Triglycol	114.8 "
Ethylene chloride		Glysantin with	
pure	208 "	tri (Prestone)	65.7 "
Glycol	565 "	Carbide	3.108 "
Diglycol	677 "	Acetaldehyde	380 "

d. Supplies Needed

Coal	<u>From:</u>	Pensberg or Hausham
Coke		Munich or other municipal cokeries
Carbide		Hart
Salt		Heilbronn near Stuttgart
Oils		Stores in Passau, Tübing and Regensburg
Toluene	{	
Benzene		
Phenol		Ruhr Territory
Ammonia		
Nitric acid	{	Middle Germany

Sulphuric acid	Kelheim near Regensburg
Nitrocellulose	Aschau
Peroxide of hydrogen	Kraiburg
Solvents	Burghausen
Plastics	Burghausen
Urea	Oppau
Formamide	Oppau
Methanol	Regensburg

e. Production Capacities in tons/month

(1) Lacquers

Luphene	35
Phtalopal	100

(2) Plasticizers

Palatinol	50
Soromine	10

(3) Plastics

Lupolene	5
Luvitherme	10

(4) Solvents

Glycol	1,000
Glycolether	
(Ethyl, butyl)	100

(5) Detergents

Leonil	50
Igepon	125

(6) Waterproofing Agents

Ramasite	20
----------	----

(7) Organic Chemicals

Ethylchloride	
techn.	90
Ethylenechloride	400
Acetaldehyde	2,000

(8) Inorganic Chemicals

Chlorine	2,500
Caustic soda	3,000

(9) Pharmaceuticals

Principal products in kg per month:

Ether	5,000
Ethylchloride	7,500
Hartosol	5,000
Postonal	1,000

Specialities in g per month:

Kresival	20,000
Zephirol	5,000
Phanodorm	1,000
Evipan	1,000
Eumarcon	500
Novocain	1,000
Adrenalin	1,000
Acetylphenothiazine	500
Avertin	1,000
Insulin	according to delivery of glands
Periston (Solution 3,5%)	according to delivery of butandiol-1,4.

f. Research

(1) Organic Section

Formation of Butadiene out of Ethanol
Glycol-ethers
Vinyl-chloride
Alcohols of Acetaldehyde
Dulcin
Textile auxiliaries
Ethylbenzene
Styrene
Polystyrene
Lacquers (Resins)
Ethylchloride
Chlorination of benzene
Chlorination of fatty acids

Polyethylene
Oxidation-experiments (ethylbenzene and others)
Rubber-compositions
Chloral
Insecticides (chloral and chlorobenzene)
Purification of crude ethylenechloride
Aldol
Ether for narcose
Crotonaldehyde
Crotonicacid

(2) Sales management

Preparation of varnishes and lacquers based upon

Nitrocellulose
Phenolic-resins
Polyvinylchlorides

Plasticizers
Solvents
Resins
Shoe-polish
Floor-polish
Glues
Esters of diglycolicacid as plasticizers
Polymerization of crude butylene
Textile auxiliaries as:

Detergents
Waterproofing-agents
Softeners

(3) Inorganic Section

Water electrolysis
Carbonmonoxide
Production of charcoal
Regeneration of potassium permanganate
Silver catalyst for formaldehyde synthesis
Basic Aluminium chloride
Phosgene (for organic synthesis)
Thionyl chloride (for organic synthesis)
Chlorosulfonic acid
Ammonium nitrate
Aluminium acetate

(4) Main Laboratory

(a) Pharmaceutical products:

Ether pro narcosi
Ethylchloride pro narcosi
Mitigal (Dimethylthianthrene)
Hartosol (Isopropylalcohol)
Kresival (Calcium salts of cresolsulfonic-acid)
Zephirol (Dimethyl-benzyl-alkyl-ammonium-chloride)
Phanodorm (5-ethyl- Δ -1-cyclohexenylbarbituric-acid)
Evipan (3.5-Dimethyl-5- Δ -1-cyclohexenyl-barbituric-acid)
Eunarcon (3-Methyl-5- Δ -bromallyl-5-isopropyl-barbituric-acid)
Novocain
Adrenalin
Acetylphenothiazine
Avertin (1.1.1-Tribromoethanol-2)
Insulin
Postonal
Abasin (1-Acetyl-3-(bromodiethyl)-acetyl-carbamide)
Periston (Poly-N-vinylpyrrolidone)
Sulfonamide:

Prontosilum album
Pyrimal
Eleudron
Eubasin

Urotropine (Hexamethylentetramine)
Camphor oil
Barium sulphate

(b) Organic Intermediates:

Formaldehyde from methanol
Ethanol from Ethylene
Octadecylalcohol from vegetable oils by high pressure hydrogenation
Higher alcohols from long chained olefines
Ester of Oxymethylvinylketone from butin-2-diol-1.4

(c) Plasticizers, lacquers and plastics section:

Resins of phenol formaldehyde (Luphen L) with
or without plasticizers
Resins of phenol acetylene for plastics
Resins of melamine formaldehyde by reaction of
dicyandiamide with melamine (nitrogen calcium)
Organic thioplastics (Thiokol a.s.o.)
Ethyl cellulose

(d) Textile auxiliaries:

Igepon A with intermediate products
Igepon T from Ethylamine including inter-
mediates.
Igepon from monoethanolamine

(e) Inorganic auxiliaries:



Interviewed: Dr. Ambros.

2. CHEMICALS MANUFACTURED FROM ACETYLENE

a. Preparation of Acetylene

Acetylene was made at Gendorf from calcium carbide produced locally (Trostberg). In spite of the high cost of the carbide (180 RM per T) it is claimed that ethylene (See b below) made from acetylene was cheaper than ethylene made from ethanol.

Acetylene was generated by both the "wet" and the "dry" gasification processes. The "wet" process, in which carbide was fed to water in an agitated vessel and the resulting lime slurry thrown away, is old and needs no further description. The generator used for the "dry" process consisted of a rotating cylinder containing an inner wire mesh cylinder about 8 inches smaller in diameter. The two cylinders rotated about an axis inclined about 8° from the horizontal after the manner of a rotary kiln drier. Carbide was fed in lumps about the size of a walnut to the upper end of the generator and was tumbled about on the rotating screen. Water was added at five different points causing the evolution of acetylene and the lumps of carbide to crumble to a dust which passed through the wire mesh inner cylinder and rode to the lower discharge end of the generator through the annulus between

the two cylinders. The $\text{Ca}(\text{OH})_2$ discharged contained about 5% water and could be readily handled by a screw conveyor. The acetylene was dried by passage over the incoming carbide, passed through cyclone dust separators and finally emerged with a purity of 98%. The chief impurity was nitrogen with which the carbide was blanketed during shipment. According to Dr. Gruber, the operation of the "dry" generator had been unsatisfactory and several difficulties (e.g. the steady feeding of the carbide) had not been eliminated.

Acetylene from carbide was pure enough for the preparation of acetaldehyde, but before it could be hydrogenated to ethylene it must be purified as follows:

- I - Scrubbed with dilute chlorine water to remove H_2S and PH_3 .
- II - Scrubbed with a solution of caustic soda to remove chlorine and for partial drying.

An attempt was made to purify the acetylene by passing it through active carbon but the process was unsuccessful and was abandoned.

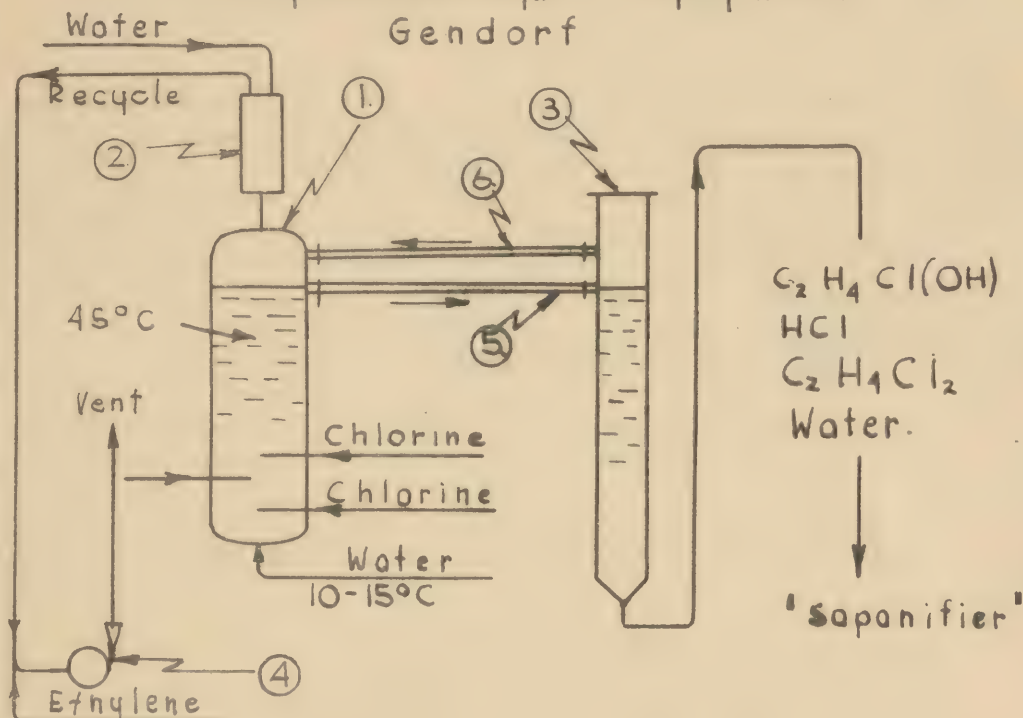
Carbide was used in the amount of 150,000 tons per year - equivalent to about 47,000 tons of acetylene.

b. Preparation of Ethylene from Acetylene

Ethylene was prepared by the hydrogenation of acetylene. The acetylene was prepared and purified as described above. The hydrogen was a mixture of electrolytic hydrogen and hydrogen prepared by the "steamiron" process. It required no purification as its chief impurity was carbon monoxide, which was hydrogenated to methane and did no harm.

The reaction was carried out in 22 converters arranged down two sides of a large building, 20 of these manifolded so that they may be operated in parallel. All the production of these 20 was passed through the other two in series for the removal of the last traces of acetylene. The converters were vertical cylinders about 10 ft. in diameter by 15 ft. high. Inside each cylinder were alternate layers of catalyst and bubble cap plates. The plates act as gas distributors and did not support any liquid. The gas mixture recycled through the converters contained about 5% acetylene, 8% hydrogen, 65% water vapor and 22% ethylene. The converters were operated at 7-10 p.s.i.g. and at a temperature of 180-320°C depending on the age and activity of the catalyst.

Figure I
Ethylene Chlorhydrin Equipment
Gendorf



- ① Reactor, Bricklined C.I. 1.6M ϕ x 12M
- ② Condenser-Scrubber; Bricklined C.I.
- ③ Still Leg - for degasification of product
- ④ Blower - to recycle gases
- ⑤ Pipe conveying liquid-gas mixture to still Leg.
- ⑥ Pipe returning gases to reactor.

The catalyst was silica gel containing traces of palladium: the exact amount of palladium not being known as the catalyst was prepared at Ludwigshafen. It was estimated at 4-6 parts per million. Catalyst life was about 12 months.

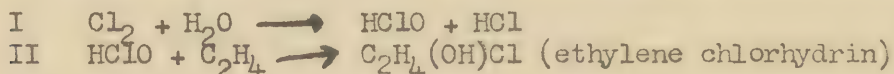
The exit gas after cooling contained 65% ethylene and was free from acetylene. It was dried over silica gel and liquefied by the Linde Process. A three column system was used. The partially liquefied mixture was fed to the middle of the first column from the bottom of which high boiling compounds (C_4-C_8) are removed. Hydrogen, methane and nitrogen were removed from the top of the second column from the bottom of which liquids passed to the side of the third column. Ethylene passed from the top of the third column and ethane from the bottom.

A second fractionation of the ethylene will give material free from ethane and having a purity of 98% but at an appreciable extra cost.

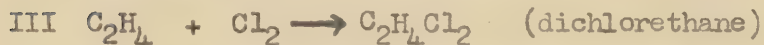
The output of the Gendorf plant was 25,000 to 30,000 T. ethylene per year.

c. Preparation of Ethylene Chlorhydrin

Ethylene chlorhydrin was prepared by the action of chlorine and water on ethylene. The equipment is sketched in Figure I. Ethylene was fed to the side of the reactor and chlorine at points above and below the ethylene. The following reactions occurred:



There was also a side reaction:



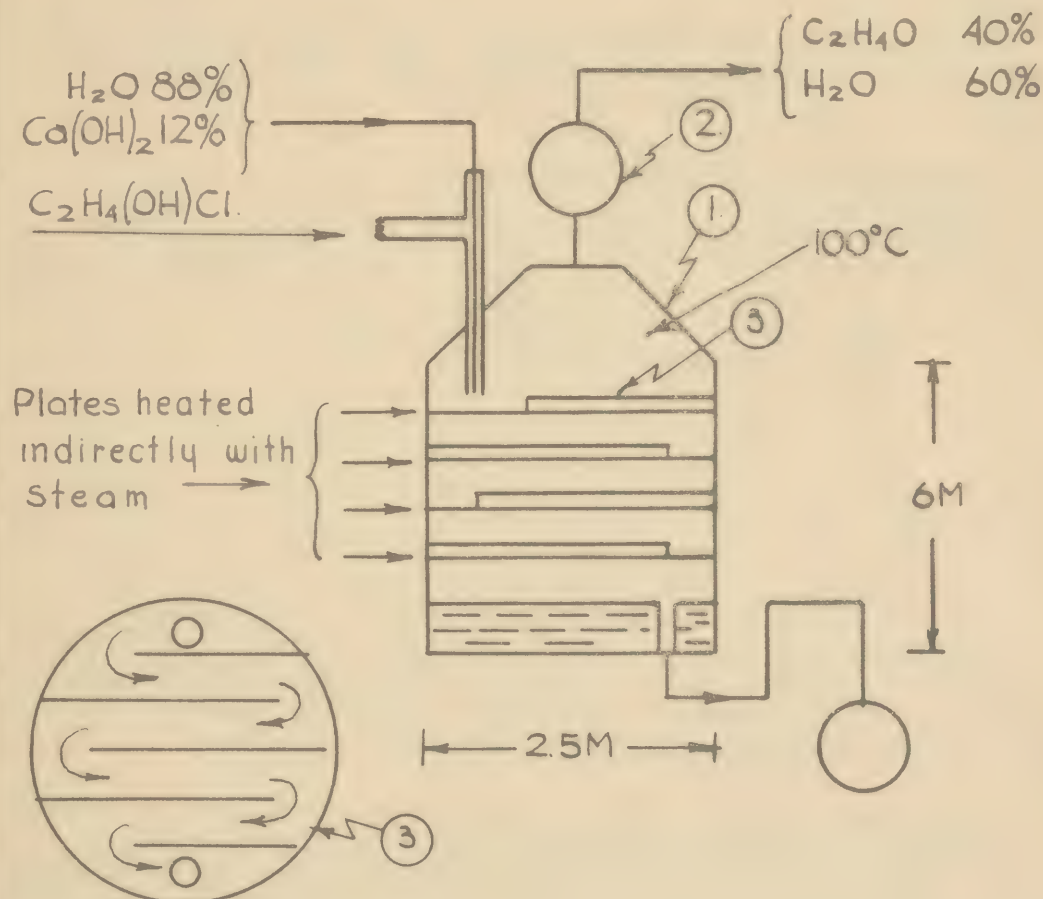
Four of the units described (Figure I) required per hour:

2000 M ³	Ethylene (gas)
1000 M ³	Water (liq.)
6000 kg	Chlorine

The chlorhydrin produced was not isolated but was hydrolyzed immediately to ethylene oxide. The yields of chlorhydrin were not known but the above feed rate produced 2.7 T. of ethylene oxide per hour.

Dichlorethane in the amount of 0.7 T. per hour was produced simultaneously.

Figure II Ethylene Oxide Equipment



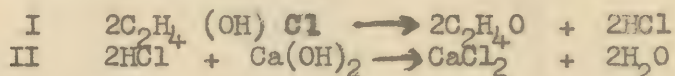
- ① Saponifier C.I. 2.5M ϕ x 6M
- ② Dephlegmator to reduce loss of water with product
- ③ Plates, steam heated, with vertical baffles to give long tortuous path for reaction mixt.

J. M^cA. H.
May 30, 1945.

Gendorf operating personnel believed that future chlorhydrin reactors should be made smaller and that all the chlorine should be introduced below the ethylene inlet to suppress the formation of dichlorethane. The latter modification is based on the theory that if all the chlorine has reacted with the water before ethylene is introduced, reactions I and II occur. If chlorine comes in direct contact with ethylene reaction III takes place.

d. Preparation of Ethylene Oxide

Ethylene oxide was prepared from the chlorhydrin by the following reaction:



The reaction was carried out in the equipment sketched in Figure II. There are four of these "saponifiers", each connected directly to one of the four chlorhydrin units described in Figure I. The chlorhydrin, HCl, water mixture and milk of lime were fed to the saponifier through concentric feed pipes in the proportion of 2 vol. chlorhydrin mixture to 1 vol. 12% $\text{Ca}(\text{OH})_2$ slurry. The resulting reaction slurry was led through a long tortuous path in the saponifier on baffled, steam heated plates as shown. Ethylene oxide and steam distilled out the top of the reactor through the dephlegmator which removed some of the steam. A calcium chloride - calcium hydroxide solution was drawn off from the bottom.

The ethylene oxide-water mixture was fractionated in a three column, continuous distillation unit. The first two columns operated in parallel and received the ethylene oxide - water mixture from the "saponifier." They contain 50 bubble cap plates and received the feed on the 17th plate. The reboilers were steam heated to 55°C. The top column temperature was 12°C. These two columns were operated with a reflux ratio of 1/1 and produced 40-50 T. per day of 98% ethylene oxide.

Residues from the first two columns were fed to a third column having a reboiler at 80°C. The water was removed from this reboiler.

Vapors from the third column were fed to the first two columns on the 33rd plate.

The yield of ethylene oxide based on ethylene amounted to 70 - 75% of the theoretical.

All three columns were made of cast iron.

Dichlorethane was removed from the bottom of the third column, washed with sulfuric acid, hydrochloric acid, and caustic soda solution and finally distilled batchwise.

e. Preparation of Glycols

Ethylene glycol was prepared by the reaction.

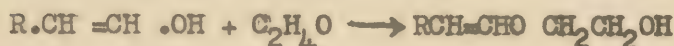


Steam and ethylene oxide were passed up through an iron column packed with steel Raschig rings. The ethylene glycol produced was purified by fractionation. By altering the temperature, pressure, and feed ratios the same equipment can be used for the production of diglycols, for example:



f. Detergents

"Leonil" detergents were made from long chain alcohols and ethylene oxide. The type reaction is:



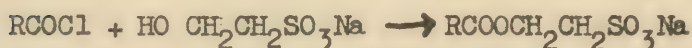
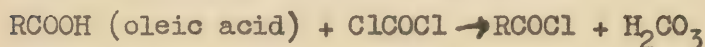
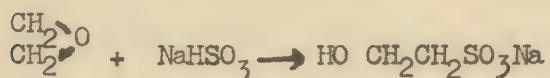
The compound made from 8 ethylene oxide molecules and one alcohol molecule is water soluble and is a detergent. The compound made from stearyl alcohol was made up as a 30% water solution and sold as "Leonil O Lsg." or Genapol. It was actually being sold in considerable quantities because of the soap shortage. As it contains no sodium it cannot form salts and may, therefore, be used with hard or soft water. It is excellent for wool scouring in either acid or neutral media. When used for domestic laundry soda is added. It does not foam and therefore does not sell readily.

As of May 19, 1945, enough raw material was available at Gendorf to prepare 42 T of Genapol (weight of water included). For subsequent production it will be necessary to prepare the fatty alcohols by hydrogenation of fatty acids.

These compounds were prepared in an enamel lined kettle under 45 p.s.i.ga. and at 165°C. The fatty acid was charged and

the ethylene oxide introduced until the batch shows the correct titre, sp.gr., mol. wt., etc.

The preparation of "Igepon O" may be outlined as follows:



"Igepon A"

"Igepon A" decomposes at about 100°C; therefore it cannot be used if laundry must be boiled.

"Igepon G" was not made from ethylene oxide. Its preparation is outlined in section 6 of this report (miscellaneous chemicals).

g. Emulsifiers

Compounds made from 20 ethylene oxide molecules and one fatty alcohol molecule are emulsifiers sold as "Emulphor C" and were used in the preparation of emulsions used for spinning wool.

One oleic acid molecule combined with 6 ethylene oxide molecules gives Emulphor A, used for emulsifying machine oils like spindle oil.

Castor oil plus 40 ethylene oxide molecules gave "Emulphor E.L."

h. Textile Aids

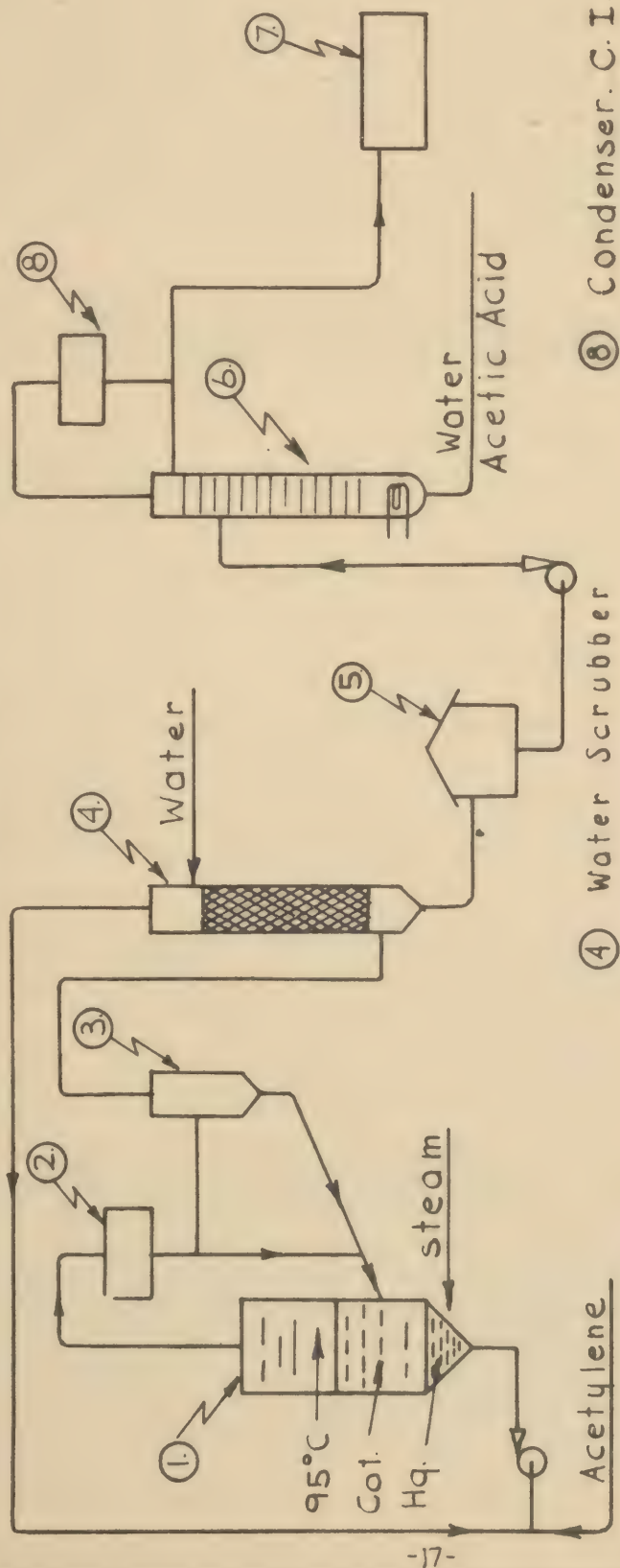
Compounds of 20 ethylene oxide molecules with one fatty alcohol molecule, were used as levelling agents for dyestuffs and were sold as "Polatinechtsolze." A 33% water solution of this material was sold as "Diazopon"; a 20% solution as "Peregal O."

Stearic acid combined with ethylene oxide gave "Soromin S.G.", which was sold as a softener for artificial silk.

i. Waxes

Waxes may be made by the polymerization of ethylene oxide - the so-called "polyethylene oxide waxes." None have been prepared at Gendorf lately.

Figure III
Acetaldehyde Equipment



① Reaction Tower

② Condenser

③ Mercury Separator

④ Water Scrubber

⑤ Dilute Aldehyde Storage

⑥ Fract. Col. - 29 Plates

⑦ Finished Prod. Storage

J. McA.H.
May 31, 1945

j. Thiodiglycol (Oxol)

The thiodiglycol plant had never been run and Dr. Hagen was unable to give any data as to production capacity. An aluminum tower, 6 m high x 0.66 m dia., packed with Raschig rings and equipped with cooling and heating coils is filled with thiodiglycol from previous manufacture. Hydrogen sulfide gas and ethylene oxide are passed in at the bottom maintaining a temperature of 90°C. The product overflows continuously to a cooler and to storage. Complete absorption of the gases is obtained.

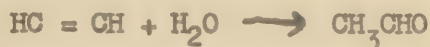
If it is desired to purify the thiodiglycol, it is dried under vacuum and treated with just enough ethylene oxide to unite with the hydrogen sulfide present as determined by titration.

k. Acetaldehyde from Acetylene

Acetaldehyde was made from acetylene in two units and the crude product was purified in a continuous fractionating column.

Production from the two units amounted to 1800 T. aldehyde per month.

The essential reaction is:



This reaction was carried out in two vertical cylinders about 2 m. diameter by 8 m. high. These cylinders are made of V2A and contain no packing. The heads are designed to act as entrainment separators.

A layer of mercury stays in the bottom of the reactor at all times. The reactor was charged with a batch consisting of:

3000 kg Fe SO₄
1600 kg H₂SO₄
8400 kg Water

Acetylene in the amount of 860 M³ per hour and under a pressure of about 25 p.s.i.g.a. was introduced below the level of the mercury which is thereby agitated until there was a mercury emulsion throughout the batch. Live steam was introduced near the bottom to help the agitation and to keep the batch temperature at about 95°C. Approximately 1 T. of steam was required per batch.

The vapors from the top of the reactor were cooled to 40°C by passage through a water cooled condenser. They then passed to a mercury separator from which mercury and condensate passed back to

the reactor tower. Mercury lost by this process amounted to 1 kg per T of aldehyde produced.

Vapors from the mercury separator passed to a water scrubber packed with Raschig rings in which the aldehyde and a trace of acetic acid were washed from the gas. The scrubbing liquor from the bottom contained about 7.5% aldehyde plus a trace of acetic acid. It was sent to a continuous fractionating column. Gases from the top of the scrubber, chiefly acetylene, were recycled to the reactor.

The aldehyde solution corresponding to an acetylene feed rate of 860 M³ per hour amounted to 21770 kg per hour. It passed through a heat exchanger, a steam heater, and was fed to the 21st plate of a 29 plate column. This column is 2 m in diameter by 10 m high, from the feed plate down, it is constructed of V2A. Above the feed plate it is cast iron. The top column temperature was 21°C, the boiling point of pure acetaldehyde. The reboiler temperature was 100°C. The residue from it was water plus a trace of acetic acid. The reflux ratio was constant at 2/1. The aldehyde taken off was degassed in a small column with a reboiler at the bottom. The acetylene recovered was put back in the recycle gas. The final product from the reboiler was 99.9% acetaldehyde.

During the reaction the ferric iron content of the catalyst solution gradually decreased until a point is reached at which conversion fell off. The catalyst was then drawn off to a settling tank in which the mercury settled out. It then passed down through a brick lined tower packed with ceramic Raschig rings in which it was blown with live steam. Next it went to a second settling tank in which more mercury was recovered, and from there to the oxidizer. In the oxidizer the ferrous iron was oxidized continuously to ferric with nitric acid. On leaving the oxidizer, the solution was dark brown due to the presence of FeSO₄.NO which was broken down by air blowing. The oxides of nitrogen from the blowing were recovered by water scrubbing in 3 towers in which the water was recycled counter current to the gas flow. The 15% nitric acid thus obtained was blended with fresh acid to a concentration of 25% and used again in the oxidizer. The catalyst solution after air blowing was ready for reuse.

3. CHEMICALS PROJECTED FROM ACETYLENE

Dr. Reppe removed his laboratory to Gendorf when it was bombed out at Ludwigshafen last fall. Dr. Reppe is a very creative research worker on the reactions of acetylene and has evolved a large number of schemes, few of which have been put into operation.

a. General Schemes for Development of Acetylene Compounds

Much of the framework of Dr. Reppe's ideas is contained in the three attached charts:

(1) Acetylene + Formaldehyde.

(a) γ -butyrolactone.

(2) Acetylene + Acetaldehyde.

b. Processes Reduced to Practice

(1) 1,4 butanediol (1,4 butylene glycol)

Several thousand tons/mo. of 1,4 butanediol were produced at Ludwigshafen, largely as an intermediate for butadiene. 1,4 butanediol was first made in a tower 18 m. high x 1.5 m. diameter containing 20 cu. m. of a contact mass of copper acetylide on silica gel where the copper compound is 10-12% of the contact mass. Five times the theoretical acetylene and formaldehyde diluted to 10% with liquor from the bottom of the tower were passed into the top of the tower under a pressure of 5 atmospheres of which 4 were due to acetylene and 1 to water vapor evaporated in the process. Temperature was 100°C. 1 cu. m. contact mass produced 1 ton of 100% butanediol per day.

The product was a 30% solution in water, which can be evaporated off and the diol crystallized from ethyl acetate. The diol can be distilled under ordinary pressure. Propargyl alcohol goes off in the first part of the distillation and can be recirculated with the formaldehyde.

The reaction is:



A side reaction to give propargyl alcohol also takes place:



Yields are:

Acetylene	92% + 4%	to propargyl alcohol
Formaldehyde	95%	

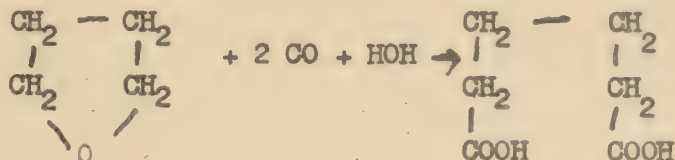
The 1,4 butanediol was hydrogenated by running it down a tower over copper nickel in the presence of hydrogen at 200-300 atmospheres and at 80-130°C. A yield of 96% to 1,4 butanediol

was obtained with the balance going to butanol. Cost of 1,4 butanediol were 60 pf/kg and it is expected that it may be reduced to 40.

c. Tetrahydrofurane and Adipic Acid

Tetrahydrofurane was produced from 1,4 butanediol in 92% yield by passing over a catalyst of phosphoric acid containing 1/2 - 1% phosphine at 260°C and 70 atmospheres pressure. The product is a good solvent and is known as Lösungsmittel T.

When tetrahydrofurane was reacted with two mols., carbon monoxide and one mol. water at 200 atm. and 270°C with 10% nickel carbonyl ($\text{Ni}(\text{CO})_4$) a yield of 90% of adipic acid was obtained.

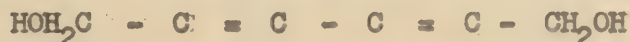


In practice the water containing 1% of its weight of iodine in the form of nickel iodide and the tetrahydrofurane in which the nickel carbonyl is dissolved were passed into the bottom of a tower with the CO gas. Adipic acid flowed out the top presumably with some tetrahydrofurane. The CO gas and nickel carbonyl passed to a separator to remove the latter and the CO returned to the tower. Throughput of the tower was 300-600 cu. m/hr. of the furane.

d. Propargyl Alcohol

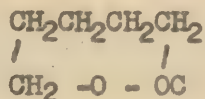
The reaction for 1,4 butinediol can be run to give 80% propargyl alcohol instead of 4% if desired. By hydrogenation with an iron catalyst under pressure, propargyl alcohol was converted to allyl alcohol and with a copper catalyst to propionaldehyde.

Oxidation of propargyl alcohol with air at 30°C over a cupric chloride catalyst gave hexadiindiol 1,6

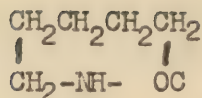


which on further reduction goes to the hexanediol 1,6.

By conversion of the hexanediol to the double aldehyde followed by an internal Canizzaro reaction ϵ -caprolactone



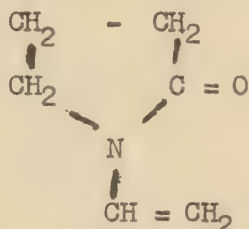
is formed which is converted with ammonia to the ϵ -caprolactam



for the polyamide known as Igamid B.

e. γ -Butyrolactone and N-vinyl Pyrrolidone

1,4 butane diol may be dehydrogenated in a tower in the presence of copper strips at 200°C to form γ butyrolactone in 96% yield. Reaction with ammonia gives a 90% yield of pyrrolidone which on treatment with acetylene furnished N-vinyl pyrrolidone in 90% yield.



The N-vinyl pyrrolidones are the bases of a new series of polymers, largely water soluble and of a character resembling albumen. They are used for glues and plastics but few uses have as yet been developed except the blood substitute "periston", described in report on the I.G. at Elberfeld. The degree of polymerization is controlled by the amount of hydrogen peroxide which is varied from 0.05 to 1.0%. The more peroxide used, the shorter is the polymer chain.

(1) Methods of Polymerization

(a) Block type

35 kg N-vinyl pyrrolidone were mixed with 150 cc 30% peroxide solution and NH_3 equivalent to 1/2 the H_2O_2 and heated to 110°C. Without further heating the temperature went to 180-190°C. The hot polymer flowed out of the kettle and was cooled in blocks. The product has a yellowish color due to the high temperature, has a low K value (30-35) and contained about 10% monomer which was extracted with ether before solution of the final product in water and filtration.

"Periston" is a 2.5% solution of a product made in this way where the temperature is kept to 70-80°C.

These products can be used as glues and binders for films, for adhesives, thickeners for emulsions and solutions, and assistants in dyeing causing darkening of the color.

(b) Solution Type

To 30 parts N-vinyl pyrrolidone in 70 parts water was added 0.5 parts 30% peroxide solution and 0.1% ammonia (100%) at 20°C. In presence of the oxygen of the air no reaction takes place, but in a stream of nitrogen it begins immediately and is complete in 2 hours. The product has a K value of 56.

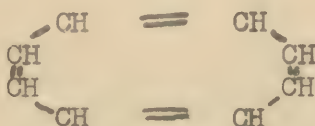
(2) Acetylene Polymers (CH₂)_n Cyclopolyolefines

By condensation of an excess of acetylene under a total pressure of 10-20 atmospheres of which 5 atmospheres is nitrogen partial pressure and in the presence of a solvent such as tetrahydrofurane, cyclooctotetraene C₈H₈ was obtained at 60-70°C in liquid phase by means of a catalyst of nickel cyanide on a carrier with a yield of 90%. The reaction took place in a tower, both gas and liquid entering at the top. The liquid product was distilled and the tetrahydrofurane returned for reuse.

Small amounts of C₁₀H₁₀ and C₁₂H₁₂, soluble resins, and cuprene were also formed and particularly by raising the temperature the proportion of these can be increased. The best temperature for C₁₀H₁₀ is 80-90°C and for C₁₂H₁₂ about 130-140°C. Azulen forms as a by product when the temperature is 80-130°C.

Cyclooctatetraene	C ₈ H ₈	BP ₇₆₀	142-143°C	Golden Yellow
Cyclodecapentaene	C ₁₀ H ₁₀	BP ₂ BP ₇₆₀	48-50°C 190-195°C	Deep Yellow
Cyclododecahexaene	C ₁₂ H ₁₂	BP _{0.5} BP ₇₆₀	60-65°C 230-235°C	Bright Yellow
Azulen	C ₁₀ H ₈	MP	99.5°C	Deep Blue

The constitutions of C₈H₈ and of Azulen are definitely determined, the former being:



The constitutions of C₁₀H₁₀ and C₁₂H₁₂ need further clarification.

The C₈H₈ and C₁₀H₁₀ have been investigated pharmacologically without finding any action. On the contrary, Prof. Kuhn

determined that the growth of certain pathogenic bacteria was completely suppressed in a dilution of 1:100,000 by the $C_{12}H_{12}$ fraction which because of small amounts of azulene (about 3%) was colored deep blue.

(3) Ethyl Alcohol

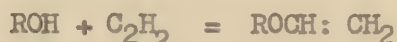
Dr. Reppe claimed that a practical process had been developed for direct hydration of ethylene which, in Germany, is likely to be produced from acetylene. The process is applicable also to propylene and butylene.

The olefine and water were run into the top of a tower packed with a catalyst consisting of a mixture of WO_2 and WO_3 made from ammonium wolframite and promoted with 5% zinc oxide. The catalyst is carried on silica gel and the mass contains 20% W. The pressure in the tower was 200-300 atmospheres and the temperature 300°C. In practice the whole system was kept under ethylene pressure as above, new ethylene being pumped in to replace that used up.

A 20% solution of ethyl alcohol flowed from the bottom of the tower to the rectifiers. The catalyst converted 1 liter ethanol per liter catalyst per hour.

(4) Acetylene and Alcohols

The type reaction for aliphatic alcohols is:



This reaction must be carried out with the alcohol in the liquid phase. The lower the molecular weight of the alcohol, the lower the optimum temperature of reaction, hence when the boiling point of the alcohol is lower than the reaction temperature, sufficient pressure must be maintained to keep the alcohol in the liquid phase.

(a) Acetaldehyde

These principles are used in the Reppe process for acetaldehyde which is not new. Methanol is treated with acetylene at 20 atmospheres pressure and 90°C to form methyl vinyl ether. By treatment of the latter with water vapor at atmospheric pressure, hydrolysis takes place to methanol and vinyl alcohol, the latter immediately rearranging to acetaldehyde. The methanol is reused. Since the process uses no mercury, which became scarce in Germany, a plant for 200 tons/month was erected in Ludwigshafen, but was bombed out after being operated for a short

while. Mercury poisoning troubles are eliminated, but Dr. Reppe admitted that the method was somewhat more expensive than the conventional mercury process.

(b) Polyvinyl oleyl Ether

The reaction of acetylene with oleyl alcohol takes place at 150-180°C with the use of 1% KOH as catalyst. No pressure is necessary. A 4 cu. m. tower capacity produced 10-20 tons/day at 99% yield. The polymerized vinyl oleyl ether is used as a pour point depressant for lubricating oils, but Dr. Reppe could furnish no details of its effectiveness.

(5) Vinyl Phenols

In the aromatic series phenols and naphthols react as follows:

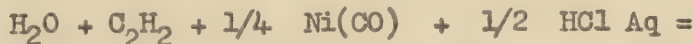


Phenol was treated with acetylene in the presence of zinc naphthenate catalyst at 10 - 20 atmospheres and about at its boiling point (182°C). The vinyl phenol polymerizes directly. By reaction of these compounds with hexamethylenetetramine a series of resins were produced with properties varying from thermo plastic to thermosetting depending on whether 1, 2 or 3 molecules of acetylene are reacted with the phenol. Koresin for synthetic rubber was made similarly, starting with butyl phenol.

(6) Acrylic Acid

Acetylene in its isoform $\text{H}_2\text{C} = \text{C} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$ reacts with CO to give methylene ketene $\text{H}_2\text{C}=\text{C}=\text{CO}$ which in turn gives $\text{H}_2\text{C}=\text{CH COOH}$, acrylic acid.

In practice the reaction runs:



Alcohols can be substituted for water to give the ester. Stoichiometric proportions of raw materials are used with the nickel carbonyl furnishing the CO; the presence of acid or halogen is necessary to bind the metal of the carbonyl as a salt. Technically 36% hydrochloric acid was used and the reaction ran

very actively at 40-42°C with practically quantitative yields of acrylic derivatives.

In the laboratory process for the preparation of ester, alcohol is placed in a three-necked flask with the conc HCl, the air is swept out with acetylene and the necessary amount of nickel carbonyl allowed to drop out of a burette. Temperature is 40-42°C. It is important that sufficient acetylene be furnished, as otherwise the rate of absorption is so great as to form a vacuum. After distillation of the acrylic ester - alcohol mixture from the nickel chloride, the acrylic ester is obtained in pure form by washing and distillation.

Regeneration of the nickel carbonyl from nickel chloride is carried out by treating the chloride solution with a slight excess of ammonia above that necessary to form the complex hexamin nickel-2-chloride and then with CO at about 80°C and 50-100 atm. The nickel carbonyl is formed quantitatively, leaving in solution the excess ammonia, ammonium chloride and ammonium carbonate.

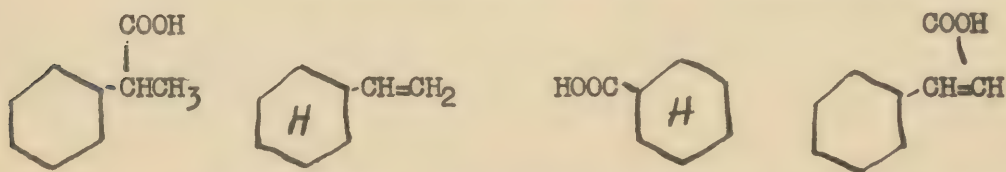
The acrylic acid process can be run continuously and without pressure except in the recovery of nickel.

(7) Products from Butadiene

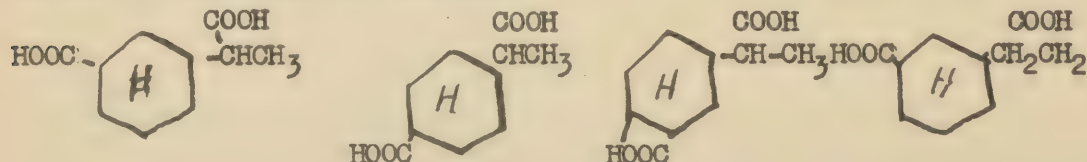
As butadiene in Germany is produced fundamentally from acetylene, Dr. Reppe's ideas on this subject are included herein.

Butadiene in benzene as a solvent is converted to vinyl cyclohexene at 270°C and 200 atmospheres with nickel carbonyl as a catalyst if no water is present. 70 - 90% yield is obtained.

In the presence of water four products are obtained:



With longer time a mixture of the following which cannot be separated is obtained:



The mixture serves as a base for plasticizers and when free of monocarboxylic acids, for polyamides.

4. APPLICATION DATA ON SURFACE COATINGS

Lacquers, varnishes, waxes and emulsions were discussed; none of these products were being made at Gendorf but were made by I.G. Farbenindustrie in Ludwigshafen. Essentially, they produced the basic materials for further processing by surface coating manufacturers.

Lacquer information possessed at the Gendorf plant is based on standard formulation using glycolesters as the active solvents for nitro cellulose, cellulose acetate, cellulose butyrate and cellulose tripropionate. The resin portion at this time is ester gum, although various synthetic resins will be employed when available. The diluent is benzene which is apparently permissible in Germany regardless of its toxicity.

Synthetic waxes were purchased from Ludwigshafen and the harder types were preferred in the 120 to 180 series, such as the palmitic esters.

Consideration is being given to the manufacture of resin emulsions and these will be based on modifications of methacrylate, polyvinylacetate and phthalic anhydride resins. Production of these products will depend upon the availability of the necessary raw materials at Gendorf.

Three grades of so-called varnishes, sold under the trade name Luphen, were made in Ludwigshafen. These are condensates of the phenol-formaldehyde type in butyl alcohol. The end product contains 75% resin and 25% butyl alcohol and is known as Luphen L. The process involves the reaction of approximately 1 part phenol, 1 part aldehyde in the presence of 4 to 6 parts butyl alcohol for 6 to 8 hours at 120 to 140°C. The addition of 1 to 5% HCl just prior to application is employed for final conversion of Luphen L resin. Ordinarily the resin solution was reduced to 50% solids with alcohol for spray purposes and was used where chemical resistance is required.

Lupen O H is Luphen L without hardener and is recommended for finishing wood or metal, either clear or pigmented.

The reaction for Luphen 145 is not carried as far as Luphen L and is soluble in ethyl alcohol. It was primarily used for can coatings which are baked at 165°C.

Chlorinated polyvinylchloride resin under the trade name Vinoplex was made at the Bitterfeld plant of I.G. Farbenindustrie. It was produced by passing chlorine gas into a 20% solution of polyvinylchloride resin (52 to 56% Cl) in carbon tetrachloride at 30 to 40°C, resulting in the addition of 2 to 4% chlorine above the theoretical amount. The dried product (Vinoplex) is a white powder which is soluble in mixed solvents of ketones and aromatics and the cast films have excellent chemical resistance. This is the basis of IGELIT-PC.

Other products which are on the agenda of the laboratory for further study are the chlorinated Buna rubbers, chlorinated polystyrenes and polyethylene resins.

The interview was with Mr. Eichstadt, Chem. Engineer.

5. PHARMACEUTICALS

The work on pharmaceuticals at Gendorf is entirely in the laboratory stage. The following notes were given as indicating the directions of work:

a. Phanodorm and Evipan

Condensation of cyclohexanone with malonic ester in the presence of piperidine acetate gives cyclohexylidene malonic ester. Cyclohexenyl ethyl (or methyl) malonic ester is obtained by treatment with sodium ethylate followed by reaction with ethyl bromide or methyl iodide. Phanodorm (MP 171°C) is produced by condensation of the ethyl compound with urea and Evipan (MP 146°) by a similar reaction of the methyl compound with methyl urea.

b. Avertin (Tribromoethyl Alcohol)

Equimolecular amounts of bromal and benzaldehyde are reacted with good cooling in the presence of about 30% on the weight of bromal of aluminum isopropylate in solution in absolute ether. After completion of the reaction, the batch is heated 1-2 hours on the water bath, the mixture is decomposed with 5% hydrobromic acid and then taken up in ether.

The ethereal solution is washed with pure water, then with dilute sodium carbonate solution and dried over sodium sulfate. After distilling off the ether the remainder is distilled under reduced pressure. Boiling Point = 92 - 94°C.

For further purification the avertin fraction is recrystallized from petroleum ether - MP = 80°C.

c. Adrenalin

The preparation of adrenalin takes place in three steps:

(1) Pyrocatechol is dissolved together with monochloroacetic acid and phosphorus oxychloride in dry benzene and boiled 24 hours under a reflux condenser. Dioxiphenyl chloromethyl ketone is formed and is obtained from the above mixture after volatilization of the benzene in vacuum and after heating up with carbon tetrachloride by crystallization from water. M.P = 173°C .

(2) The powdered dioxiphenyl chlormethyl ketone in alcohol suspension is shaken with a 40% aqueous solution of methyl amine for 24 hours, then filtered and washed with cold alcohol. The 4-methyl amino acetopyrocatechol formed is purified by solution in hydrochloric acid and reprecipitation with ammonia. The decomposition point is 230°C .

(3) In the last step the above compound is reduced, either in the presence of aluminum amalgam or electrocatalytically by means of a nickel or palladium electrode and addition of a palladium chloride solution, to the optically inactive d,l adrenalin.

The inactive forms can be separated by means of the bitartrates into the optically active components.

d. Eunarcon

N-methyl-5 isopropyl bromoalkyl barbituric acid.

Molar amounts of isopropyl bromide and sodium malonic ester are reacted. The isopropyl malonic diethyl ester is again converted to the sodium compound and decomposed with α bromoalkyl bromide to isopropyl bromoalkyl malonic diethyl ester. The preparation of the α bromoalkyl bromide takes place according to the publication of Von Tollens by decomposition of 1, 2, 3 tribromopropane in ether solution with sodium. By condensation of the isopropyl α bromoalkyl malonic diethyl ester with methyl urea, ring closure takes place to N-methyl-5-isopropyl bromoalkyl barbituric acid.

e. Insulin

Extraction of the comminuted pancreas glands with dilute 60% alcohol containing HCl is followed by filtration and precipitation of impurities by ammonia. Sulfuric acid is added and the alcohol distilled off in vacuum at a maximum temperature of 30°C . The insulin is fractionally precipitated from the aqueous solution with salt and finally by repeated precipitation at the isoelectric point. The insulin is crystallized from phosphate buffer solution after addition of zinc chloride.

f. Zephirol

Dimethyl benzoyl alkyl ammonium chloride.

A fatty alcohol such as octadecylalcohol is converted at 130°C in a corrosion-resisting autoclave with dry HCl gas under pressure to the corresponding alkyl chloride. The chlorohydrocarbon purified by distillation under high vacuum is brought into reaction at $100-150^{\circ}\text{C}$ with 1.5 mols. dimethylamine in benzene solution. The hydrochloride obtained is crystallized from alcohol, slurried with ether and the free amine prepared by shaking with caustic potash solution. Finally the nitrogen of the dimethylamino octadecane is converted to quaternary by addition of 1 mol. of benzyl chloride.

g. Mitigal

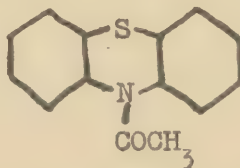
Dimethylthianthrene.

A solution of 600 gms SCl_2 in 1.2 liters toluene is allowed to flow into 2.8 liters of ~~toluene~~² and 400 gms aluminum chloride with heavy stirring. Stirring is continued at room temperature. The reaction product is poured on to ice and separated. The excess toluene is removed thru steam distillation and the reaction mixture given a fractional distillation. Chief product $\text{BP}_3 = 170 - 180^{\circ}$.

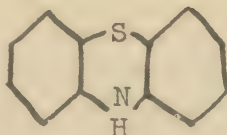
h. Novocaine

p-nitro benzoyl chloride is condensed with diethylamino ethanol in boiling benzene. The p-nitrobenzoic diethylamino ethyl ester is reduced with a chrome nickel catalyst at 2 atmospheres pressure. The amino compound is converted into the hydrochloride, Novocaine.

i. N-Acetylphenothiazine



A mixture of diphenylamine and sulfur is heated whereby phenothiazine is obtained.

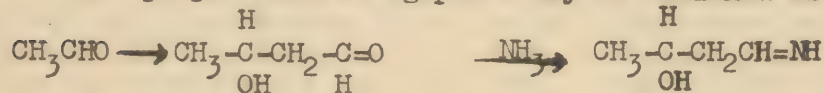


This is heated with acetic anhydride, whereby the nitrogen is acetylated. Actually a mixture of diphenylamine, sulfur and acetic anhydride can be heated together, and also obtain the N-acetylphenothiazine.

6. MISCELLANEOUS ITEMS

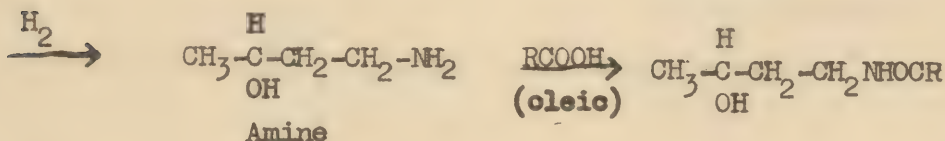
a. Igepon G.

The preparation of Igepon G may be outlined as follows:

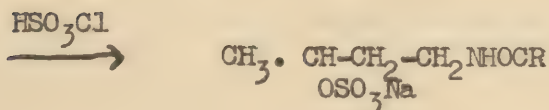


Acetaldehyde Aldol

Aldimine



Amine



"Igepon G"

b. Water Softener - "Trilon"

The sodium salt of the compound prepared by the reaction

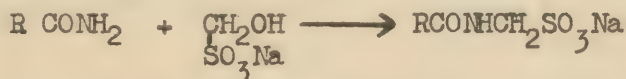


is a water softener sold as "Trilon."

Manufacture was started at Ludwigshafen just before the war.

c. Detergent

Dr. Reppe spoke of work done on a detergent developed by the Japanese, Dr. Otta, with whom, however, he claimed to have no direct contact. The product is made by reaction of a fatty acid amide and formaldehyde - sulfite -



This is not as good as the Igepon but is cheaper and easier to manufacture.

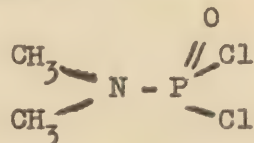
d. Ramasite

Ramasite is a water proofing agent consisting of an emulsion of paraffins (from brown coal) of different types hard and soft with less than 1% Nekal with a solution of basic aluminum acetate (or formate or chloride) and urea.

For use the emulsion is diluted 1 to 10 or 20 with water and the fabric drenched, then dried at over 100°C for the formates but at 70°C for the acetates. The water proofing effect is stated to be better than Velan (Zelan) but is removed by washing.

e. Blattan

Dr. Ambros mentioned a contact insecticide developed by Dr. Schroeder at Elberfeld -



f. Polystyrene

A styrene polymerization tower had been shipped from Ludwigshafen to Gendorf and was lying in the freight yard. It was built of five steam jacketed sections and contained two steam coils in the lower sections. In practice the monomer styrene would pass to two prepolymerization kettles in parallel where it would be held with stirring at 50 - 80°C for two days without catalyst. From these kettles it passed to the top of the tower at 70°C and flowed slowly thru with a total time of sojourn in the tower of 24 hours. The temperature down the tower gradually rose to 200°C at the conical exit which was heated electrically. The tower was estimated to be 15 feet high x 2.5 feet diameter and to produce 1 ton polystyrene per day. From the conical outlet the molten polymer passed thru an electrically heated screw conveyor to a continuous metal belt carried on cooled rollers where it solidified and passed to the guiding system.

The chief grades of polystyrene produced were No. 3 with a molecular weight of 100,000 and No. 4 of 200,000. The No. 3 grade being the most important. It was stated that the styrene is completely polymerized.

CHART 1

ACETYLENE + FORMALDEHYDE

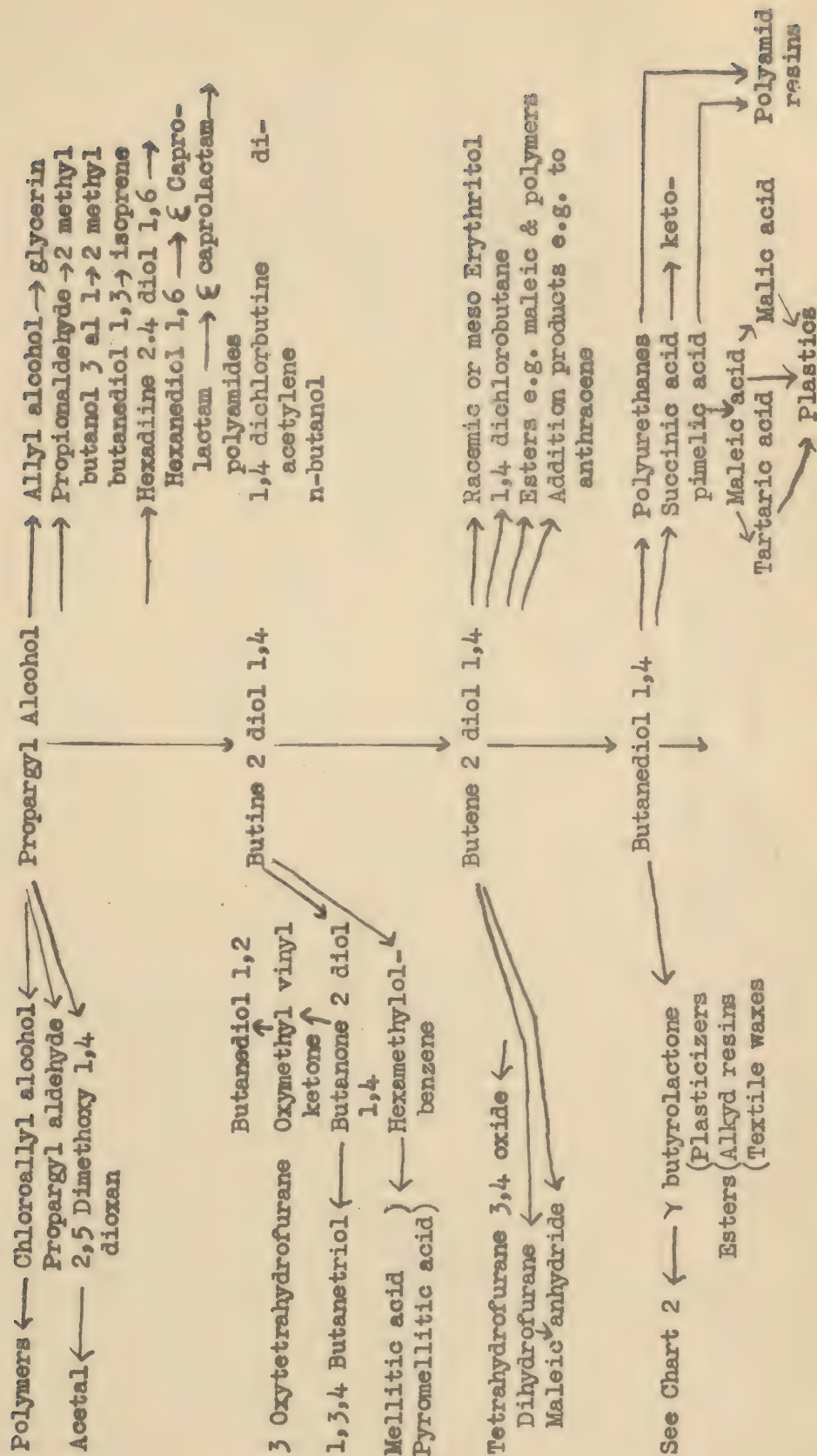


CHART 1 (Continued)

ACETYLENE + FORMALDEHYDE

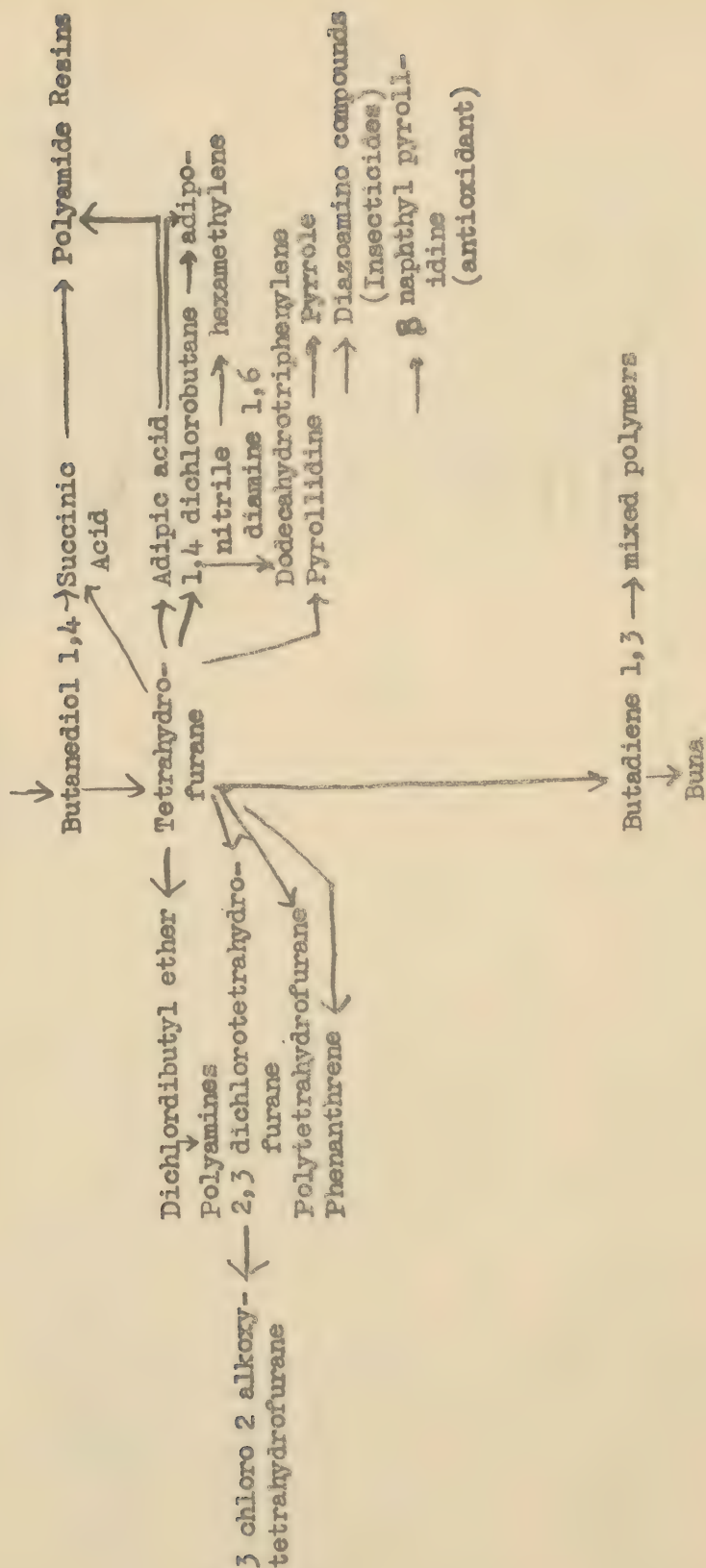


CHART 1 A

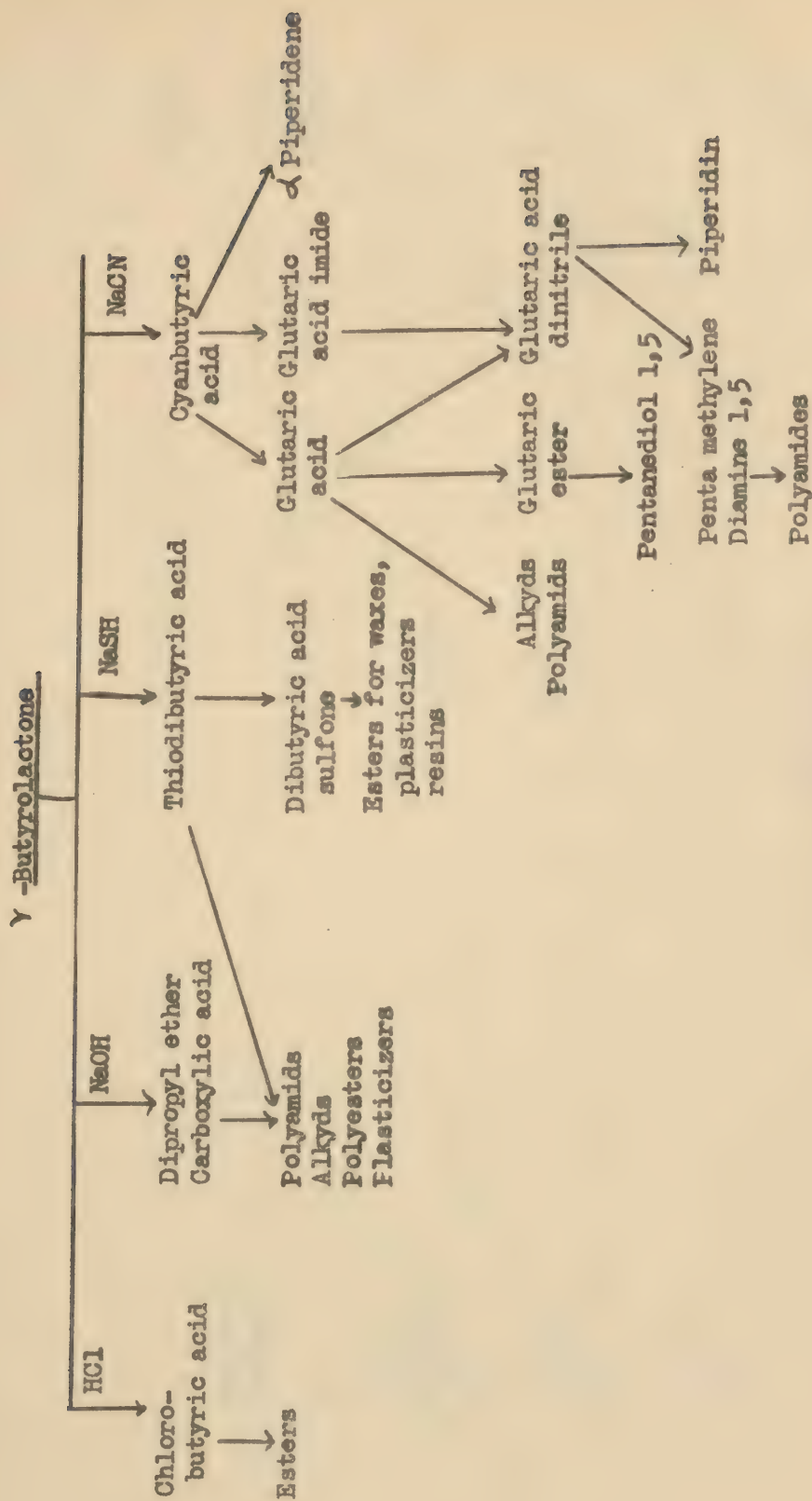


CHART 1 A (Continued)

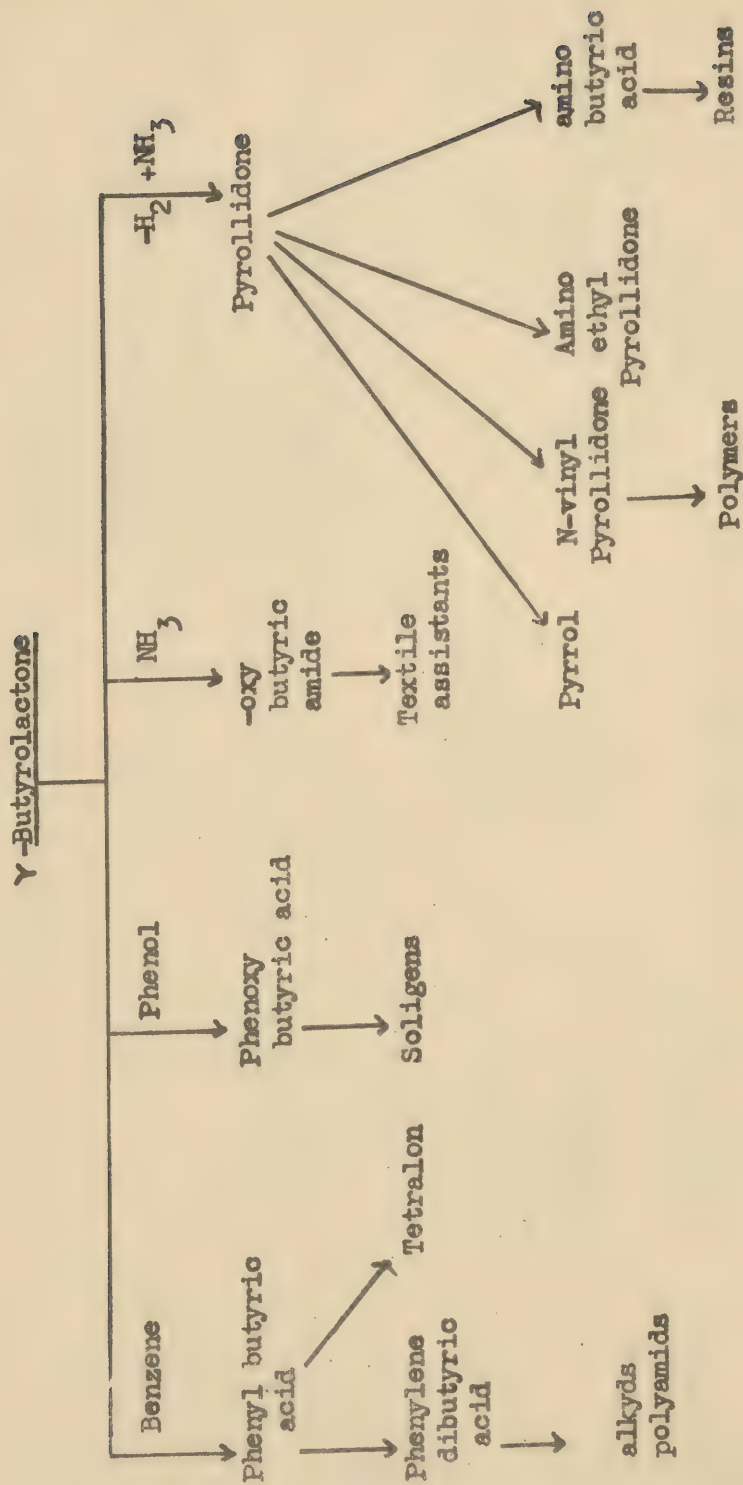
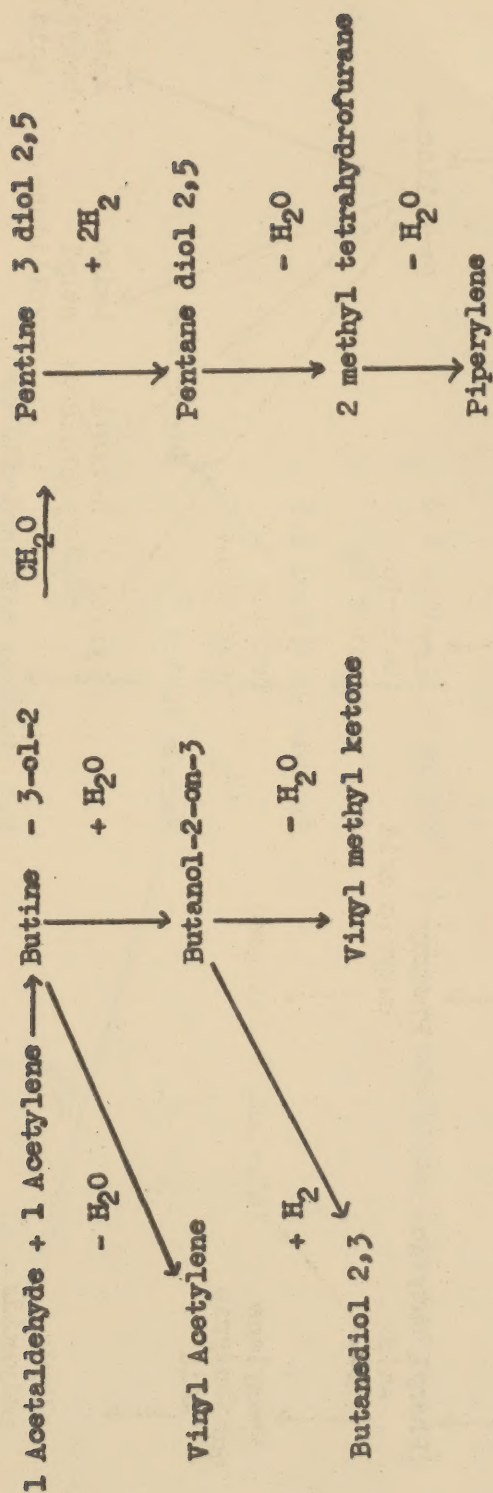
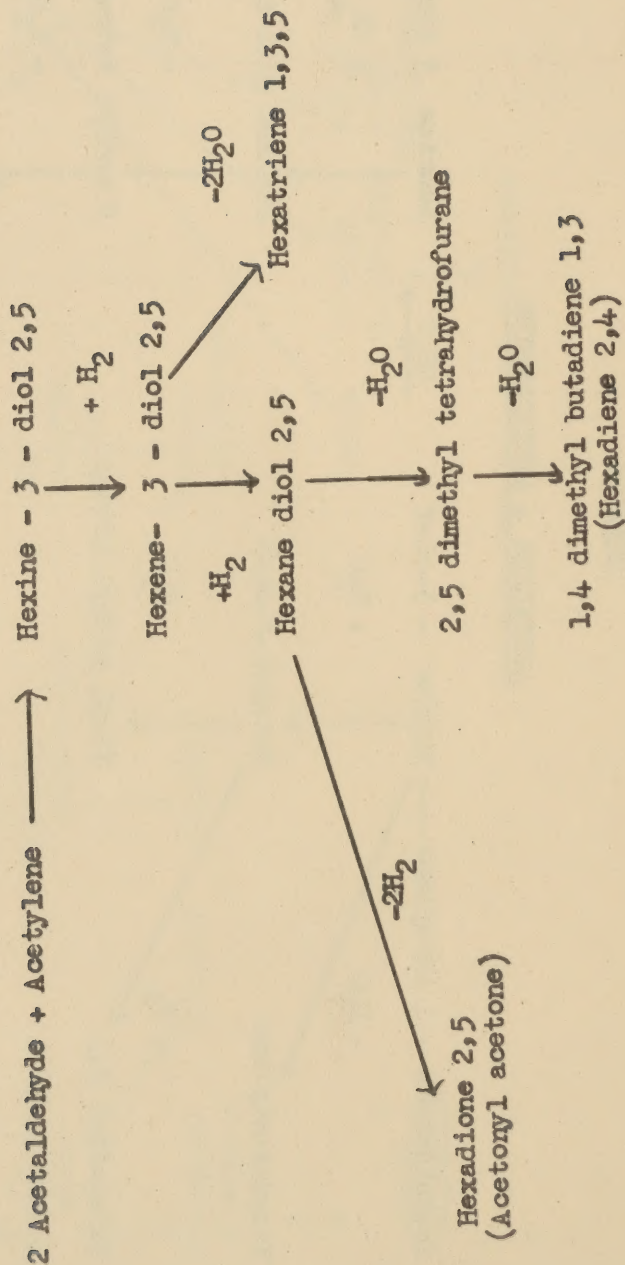


CHART 2

ACETYLENE + ACETALDEHYDE



- 38 -



NATIONAL LIBRARY OF MEDICINE



NLM 03617448 9